

Express Mail #EI568916187US

Atty. Dkt. No.: LIT-PI-099

**Title:       PROCESS FOR PRODUCING BIODIESEL LUBRICANTS, AND FUEL AND  
LUBRICANT ADDITIVES IN A CRITICAL FLUID MEDIUM**

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**PROCESS FOR PRODUCING BIODIESEL LUBRICANTS, AND FUEL****AND LUBRICANT ADDITIVES IN A CRITICAL FLUID MEDIUM****CONTRACTUAL ORIGIN OF THE INVENTION**

This invention was made with United States Government support under Contract No. DE-AC07-94ID13223, now Contract No. DE-AC07-99ID13727 awarded by the United States Department of Energy. The United States Government has certain rights in the invention.

**RELATED APPLICATION**

This application claims priority from PCT application S/N PCT/US99/16669 filed July 22, 1999 which claims priority from United States provisional application S/N 60/094,076 filed July 24, 1998.

**BACKGROUND OF THE INVENTION****Field of the Invention**

The present invention relates to a process for producing biofuels as alternatives or additives to currently used petroleum-based automotive or other vehicular fuels and lubricants by reacting fats and oils such as triglycerides and free fatty acids in a single critical phase to provide increased reaction rates and decrease the loss of catalyst or catalyst activity. The invention includes the transesterification of triglyceride- containing substances and esterification of free fatty acid- containing substances with alcohol to

1 produce alkyl esters of triglycerides, a desirable additive or alternative for petroleum  
2 diesel fuel or lubricants.  
3

#### 4 **Description of the Prior Art**

5 Significant quantities of esters such as triglycerides and free fatty acids are  
6 available from inexpensive feedstocks such as, animal fats, vegetable oils, rendered fats,  
7 restaurant grease and waste industrial frying oils. The triglyceride esters can be reacted,  
8 or transesterified, with alcohol to produce glycerol and the alkyl esters, and the free fatty  
9 acid can be reacted, or esterified, with alcohol or water to produce the alkyl ester. These  
10 alkyl esters create desirable additives or alternatives to petroleum diesel fuel as well as  
11 other high value end products such as detergent surfactants, herbicides, pesticide diluents,  
12 sticking agents, or lubricating additives for hydraulic and transmission fluids to name a  
13 few. Consequently, numerous patents exist dealing with processes surrounding  
14 transesterification of triglycerides and esterification of free fatty acids with alcohols such  
15 as methanol, ethanol or butanol to create the corresponding alkyl esters. U. S. Patents  
16 5,713,965 and 5,525,126, incorporated herein by reference, are examples of such  
17 processes.

18 The transesterification or esterification reaction is normally carried out in an  
19 excess of the stoichiometric quantity of alcohol and a catalyst, usually a base such as  
20 potassium hydroxide although, the reaction can also proceed with an acid catalyst as well.  
21 In addition to creation of the alkyl esters, the transesterification reaction also produces  
22 glycerol.

1 Traditionally, triglyceride transesterification requires a multiple step process with  
2 one or more batch reactors. Initially, the triglycerides and alcohol form two immiscible  
3 liquid phases. As the reaction proceeds, two separate liquid phases form. One contains  
4 the newly formed alkyl esters of the triglyceride and the other the glycerol with the  
5 excess alcohol, catalyst and feed oil being dispersed into both phases. The reaction time  
6 for each step typically is measured in hours and once completed the liquid products must  
7 be allowed sufficient time to separate phases before additional processing and separation  
8 steps can occur to produce the final products. Excess alcohol must be recycled and the  
9 unused catalyst typically must be neutralized.

10 Even the most efficient of the traditional processes require multiple hours to  
11 process each batch of feed. Additionally, significant problems arise in the separation  
12 steps. Significant quantities of glycerol left in the alkyl esters diminishes the quality of  
13 the diesel fuel and likewise contaminated glycerol also loses much of its value compared  
14 to pure uncontaminated glycerol. Traditionally the separation procedures necessary to  
15 adequately clean the two product streams produces large quantities of waste water  
16 thereby creating additional cost and/or process complexity.

## 17 18 **SUMMARY AND OBJECTS OF THE INVENTION**

19 This invention provides a single-phase process for producing alkyl esters useful as  
20 biofuels and lubricants by the reactions of triglyceride esters and free fatty acids. This  
21 invention teaches a process where the reactants enter a reactor, whether batch or  
22 continuous, dissolved in a critical fluid. The critical fluid provides a single-phase

1 medium in which diffusion of the reactants into different liquid phases is eliminated, and  
2 mass transfer limitations are essentially eliminated thereby increasing the overall reaction  
3 rate. A critical fluid is a fluid whose temperature is within 20% of the critical  
4 temperature of the fluid as measured in Kelvin and pressure within 0.5-15 times the  
5 critical pressure as modified by any co-solvent.

6         Additionally, the solubility of the reaction products such as alkyl esters in the  
7 critical fluid can be controlled by controlling the reactor's temperature and pressure.  
8 Where a reaction product's solubility is low or nonexistent such as glycerol it drops out of  
9 the fluid as it is created, thereby driving the reaction equilibrium toward product  
10 production which significantly reduces the quantity of excess reactants such as alcohol  
11 needed to drive the reaction to completion.

12         The use of a critical fluid also allows for a wide range of catalysts, both liquid  
13 phase and reusable solid phase acid or base catalysts. Solid phase catalysts have  
14 significant additional advantages by limiting unwanted side reactions and producing  
15 higher conversion rates of the desired products.

16         With the reaction completed, the critical fluid medium also facilitates clean,  
17 efficient separations. The reaction products typically can be sequentially and selectively  
18 removed from the critical fluid medium by adjusting the temperature and pressure of the  
19 critical fluid medium. In a transesterification reaction of triglycerides, the glycerol is  
20 removed first leaving the alcohol esters in the critical fluid. With the glycerol removed,  
21 the temperature and pressure is again changed to drop out the alkyl esters. Once the

1 products are removed the critical fluid and any excess reactants are returned to the  
2 beginning of the process.

3 It is the object of the present invention to provide a process for reacting  
4 triglyceride- and free fatty acid- containing substances capable of completing the reaction  
5 in significantly less time than present conventional processes.

6 It is another object of the present invention to provide a process for reacting  
7 triglyceride- and free fatty acid- containing substances capable of using reusable catalyst  
8 thereby avoiding the need for process neutralization.

9 It is yet another object of the present invention to provide a process for reacting  
10 triglyceride- and free fatty acid- containing substances capable of using a solid phase  
11 catalyst.

12 It is yet another object of the present invention to provide a process for reacting  
13 triglyceride- and free fatty acid- containing substances with higher yields of desired  
14 product over conventional processes.

15 It is yet another object of the present invention to provide a process for reacting  
16 triglyceride- and free fatty acid- containing substances capable of operating in a single  
17 phase, thereby eliminating immiscible liquid phases and reducing mass transfer reaction  
18 limitations.

19 It is yet another object of the present invention to provide a process for reacting  
20 triglyceride- and free fatty acid- containing substances with improved separation  
21 capabilities for separating purified reaction products without the need for washing steps.

1 It is yet another object of the present invention to provide a process for reacting  
2 triglycerides and free fatty acids which can quantitatively react the triglycerides or free  
3 fatty acids with significantly less excess alcohol than present processes.  
4

#### 5 **BRIEF DESCRIPTION OF THE DRAWINGS**

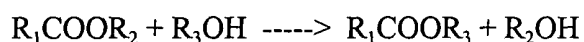
6 In order that the manner in which the above-recited and other advantages and  
7 objects of the invention are obtained, a more particular description of the invention  
8 briefly described above will be rendered by reference to specific embodiments thereof  
9 which are illustrated in the appended drawings. Understanding that these drawings depict  
10 only typical embodiments of the invention and are not therefore to be considered to be  
11 limiting of its scope, the invention will be described and explained with additional  
12 specificity and detail through the use of the accompanying drawings in which:

13 Figure 1 is a simplified flow diagram which illustrates an embodiment of the  
14 invention employing a continuous reactor.  
15

#### 16 **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

17 The present invention describes a process for reacting organic compounds having  
18 the generic formula  $R_1COOR_2$  with short-chain ( $C_1$  to  $C_4$ ) alcohols in a single critical  
19 fluid phase medium over an acidic or basic catalyst to produce alkyl esters suitable as a  
20 biodiesel fuel. One skilled in the art will recognize that organic compounds from the  
21 family of compounds known as acylglycerols, fats, oils, waxes, or free fatty acids have  
22 the general formula  $R_1COOR_2$ . One skilled in the art will also recognize that

acylglycerols can be mono, di, or tri substituted in any manner. The invention includes the transesterification and esterification of  $R_1COOR_2$  molecules with short-chain alcohols such as methanol, ethanol, propanol, or butanol to produce alcohol esters. The invention also encompasses the acid and base catalyzed hydrolysis of  $R_1COOR_2$  compounds in a single critical fluid medium where  $R_1$  is a chain of aliphatic hydrocarbons ( $C_4$  to  $C_{36}$ ), and where  $R_2$  can either be glycerol or can be another aliphatic hydrocarbon chain ( $C_4$  to  $C_{36}$ ) linked to  $R_1$  via the carboxylic ester ( $BCOO-$ ) linkage. The reaction is generally described as follows:



catalyst

In the case of mono-, di-, and triglycerides, fats and oils,  $R_1$  is the aliphatic hydrocarbon ( $C_4$  to  $C_{24}$ ) chain,  $R_2$  is glycerol and  $R_3$  is a hydrocarbon group, and preferably short chain alkyl group, more preferably methyl, ethyl, propyl, or butyl group attached to the alcohol.

In the case of free fatty acids,  $R_1$  is the aliphatic hydrocarbon chain wherein the terminal carboxylic acid group could be  $R_1COO^-$ , or  $R_1COOH$ , or  $R_1COO^- M^+$  where  $M^+$  is a metal (thus, the salt of a fatty acid); and,  $R_3$  is the short-chain hydrocarbon attached to the alcohol. In the case of a wax,  $R_1$  is an aliphatic hydrocarbon chain linked to  $R_2$  via the carboxylic ester linkage, and  $R_3$  is the short-chain hydrocarbon attached to the alcohol.

Figure 1 provides a basic flow diagram for the glyceride reaction process employing a continuous reactor. Throughout the description of the process diagram, the various process vessels will be numbered between 1 and 99, with the various process streams being numbered beginning with 100. While the following discussion will



1 describe a continuous reactor process for a transesterification reaction of glycerides with  
2 an alcohol ROH, one skilled in the art will recognize the process principles apply equally  
3 well in other process settings such as ones using batch reactors and separation processes  
4 as well as reactions producing alternate products to the alcohol esters as well as processes  
5 beginning with fatty acid feeds.

6 A glyceride containing feed 100 is mixed with an input alcohol stream 102. The  
7 choice of alcohol will be a function of the desired reaction product, and typically such  
8 alcohols as methanol, ethanol, propanol and butanol are chosen for practical reasons,  
9 however, one skilled in the art will readily recognize the flexibility of choices and non-  
10 limiting aspect of the above list. This input alcohol stream 102 contains approximately a  
11 stoichiometric quantity of alcohol necessary to quantitatively react the input glyceride  
12 feed 100. While the reaction will require some excess alcohol, that needed excess is  
13 contained in a critical fluid recycle stream 104 which provides a transport medium that  
14 solvates the reactants to create the required process conditions. The exact critical fluid  
15 employed for a given reaction will depend on specifically chosen process parameters such  
16 as temperature, pressure, desired reaction products, solubility of the reaction products,  
17 quantity of excess alcohol needed to drive the reaction to completion, post reaction  
18 separation processes and chosen catalyst. Examples of possible critical fluid solvents are  
19 carbon dioxide, sulfur dioxide, methane, ethane, propane, or mixtures thereof, with or  
20 without critical fluid co-solvents such as methanol, ethanol, butanol or water. Naturally,  
21 to the extent quantities of the critical fluid are lost during the process they can be  
22 replenished with a critical fluid make-up stream 106.

1 The mixing of the input feed 100 (substance containing free fatty acids and/or  
2 glycerides), the input alcohol 102, the critical fluid recycle 104 and critical fluid make-up  
3 106 streams creates a reactant input stream 108 which is fed into a continuous reactor 10.  
4 The temperature and pressure of the reactant input stream will depend on its components  
5 and the desired process parameters. The important criteria for the critical fluid is its  
6 ability to dissolve the reactants. Reaction temperatures should be within 20% of the  
7 critical temperature of the fluid as measured in Kelvin, and pressures within 0.5-15 times  
8 critical pressure as modified by any co-solvent. Reaction temperatures are typically in  
9 the range from about 20 to 200 degrees C with reaction pressures in the range from about  
10 150 psig to 4000 psig.

11 The transesterification reaction generally proceeds in the presence of a catalyst,  
12 either acidic or basic. Liquid acids and bases, such as the common inorganic acids HCl,  
13 H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> and inorganic bases NaOH and KOH typically provide the needed  
14 catalytic activity. Additionally, the use of a critical fluid medium allows for use of a  
15 solid phase catalysts with either acidic or basic surfaces such as microporous crystalline  
16 solids, such as zeolites, and non-crystalline inorganic oxides such as alumina, silica,  
17 silica-alumina, boria, oxides of phosphorus, titanium dioxide, zirconium dioxide,  
18 chromia, zinc oxide, magnesia, calcium oxide, iron oxides, unmodified, or modified with  
19 chlorine, fluorine, sulfur or an acid or base, as well as mixtures of the above group or an  
20 exchange resin with either acidic or basic properties. Where solid catalysts are used in  
21 the reactor 10, they may create a catalytic packed bed or float free inside the reactor.

1 As the reaction proceeds, glycerol and the alkyl esters of the glyceride are  
2 produced. Glycerol has low solubility in critical fluids such as CO<sub>2</sub> and propane which  
3 will cause the glycerol product to drop out of the critical fluid medium. This removal of  
4 the glycerol from the reaction phase of the critical fluid medium will enhance the reaction  
5 equilibrium and drive the reaction further to completion with limited excess alcohol. One  
6 skilled in the art will then recognize that the quantity of excess alcohol required to drive  
7 the reaction to completion will depend not only on such factors as the desired reaction  
8 rate, but also the glycerol solubility in the chosen critical fluid.

9 The ability of the critical fluid medium to solvate the reactants eliminates the  
10 immiscible phases found in conventional processes. The single phase reaction eliminates  
11 inter-phase mass transfer of the individual reactants and catalyst, thereby greatly  
12 increasing the reaction's rate.

13 After completion of the reaction the reaction vessel may be the separation vessel,  
14 a final product stream 110 exits the reactor 10 and enters a first product separator 12. In  
15 the first product separator 12 the product stream's temperature and/or pressure are  
16 modified to allow the least soluble product in the critical fluid to quantitatively drop out,  
17 the glycerol in this embodiment. Once the glycerol has dropped out of the critical fluid  
18 medium, a physical separation of the two phases can be readily accomplished. A glycerol  
19 product stream 112 and a glycerol depleted product stream 114 exists the first separator  
20 12. The glycerol depleted product stream 112 consists of the critical fluid, excess  
21 alcohol, alcohol ester of the glycerides and any remaining catalyst, if a liquid catalyst is  
22 used, and then enters a second product separator 14. Again the temperature and pressure

1 of the critical fluid are lowered to allow the desired product, the alkyl ester of the  
2 glyceride of this embodiment, to drop out of the critical fluid while retaining the excess  
3 alcohol in the critical fluid. The physical separation of the two phases then creates a  
4 second product stream of the alcohol ester 116 and the critical fluid recycle 104 which  
5 will be reintroduced back into the front of the process after having its pressure and  
6 temperature restored to the original input reaction requirements.

7 While this embodiment describes a process with two product streams, the glycerol  
8 and alkyl ester, it should also be apparent to one skilled in the art that a reaction  
9 producing more than two products can produce multiple product streams by simply  
10 increasing the number of product separators.

11 Although the present invention has been described with reference to preferred  
12 embodiments, those skilled in the art will recognize that changes may be made in form  
13 and detail without departing from the spirit and scope of the invention.